

534 Rec'd PCT/PTC 21 JUN 2000

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo-5766/LeA 32,756

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

To be assigned 09/582141

INTERNATIONAL APPLICATION NO.

PCT/EP98/08073

INTERNATIONAL FILING DATE

December 10, 1998

PRIORITY DATE CLAIMED

December 23, 1997

TITLE OF INVENTION

IMPROVED DOUBLE-METAL CYANIDE CATALYSTS FOR THE ...

APPLICANT(S) FOR DO/EO/US

Jörg Hofmann et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(l).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
- a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
- b. ☐ has been transmitted by the International Bureau.
- c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
- a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
- b. ☐ have been transmitted by the International Bureau.
- c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
- d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
- ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information: Abstract; Form PTO 1449 w/references

17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5))

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$970.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$840.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO but
international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$760.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(1)-(4) \$96.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

\$ 840.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(c)).

\$

CLAIMS NUMBER FILED NUMBER EXTRA RATE

Total claims 8 -20 = X \$18.00 \$

Independent claims 1 -3 = X \$78.00 \$

MULTIPLE DEPENDENT CLAIM(S) (if applicable) +\$260.00 \$

TOTAL OF ABOVE CALCULATIONS = \$

Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).

\$

SUBTOTAL = \$

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE = \$ 840.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + \$ 40.00

TOTAL FEES ENCLOSED = \$

Amount to be:

refunded \$

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a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 880.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Bayer Corporation
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100 Bayer Road
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00157

PATENT - TRADEMARK OFFICE

SIGNATURE

Carolyn M. Sloane

NAME

44,339

REGISTRATION NUMBER

09/582141

534 Rec'd PCT/PTC 21 JUN2000

PATENT APPLICATION
Mo 5766
LeA 32,756

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
JÖRG HOFMANN ET AL) PCT/EP98/08073
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: IMPROVED DOUBLE-METAL)
CYANIDE CATALYSTS FOR)
THE PRODUCTION OF POLY-)
ETHER POLYOLS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please enter the following amendments and consider the following remarks in support of the above-referenced application:

IN THE TITLE:

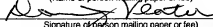
On page 1, lines 1-2, please delete the words "Improved double-metal cyanide catalysts for the preparation of polyether-polyols" and insert therein --IMPROVED DOUBLE-METAL CYANIDE CATALYSTS FOR THE PRODUCTION OF POLYETHER POLYOLS--.

"Express Mail" mailing label number EK983331625US
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Donna J. Veatch

(Name of person mailing paper or fee)



Signature of person mailing paper or fee)

IN THE ABSTRACT:

On page 22, please delete the title which reads "Improved double-metal cyanide catalysts for the preparation of polyether-polyols" and insert therein --IMPROVED DOUBLE-METAL CYANIDE CATALYSTS FOR THE PRODUCTION OF POLYETHER POLYOLS--.

IN THE CLAIMS:

Please cancel Claim 8.

Please amend Claims 1-7 as follows.

1. (Amended) A [D]~~double-metal cyanide (DMC) catalyst[s] comprising:~~

a) a double metal cyanide compound;

[and]

b) an organic complexing ligand;

and [characterized in that they contain]

c) 2 to 80 wt. % of a polycarbonate, based on the amount of finished catalyst.

2. (Amended) The DMC catalyst[s] according to Claim 1, [characterized in that] in which the double-metal cyanide compound is zinc hexacyanocobaltate(III).

3. (Amended) The DMC catalyst[s] according to Claim 1, [characterized in that] in which the organic complexing ligand is tert-butanol.

4. (Amended) The DMC catalyst[s] according to [Claims] Claim 1 [to 3], [characterized in that they contain] in which from about 5 to 50 wt. % of a polycarbonate is present.

5. (Amended) The DMC catalyst[s] according to [Claims] Claim 1 [to 4], [characterized in that they contain] further comprising an aliphatic polycarbonate[s] having a hydroxyl end group[s] and an average molecular weight[s] below 12,000, as determined by measurement of the OH number, which [are] is obtainable by reacting a polyfunctional aliphatic hydroxyl compound[s] with diaryl carbonate, dialkyl carbonate, a dioxolanone[s], phosgene, a bischlorocarbonic acid ester[s] or urea.

6. (Amended) The DMC catalyst[s] according to [Claims] Claim 1 [to 5], [characterized in that they contain] further comprising an aliphatic polycarbonate-diol[s] with an average molecular weight[s] of 400 to 6000, as determined by measurement of the OH number, which [are] is obtainable by reacting a non-vincinal diol[s] with diaryl carbonate, dialkyl carbonate, a dioxolanone[s], phosgene, a bischlorocarbonic acid ester[s] or urea.

7. (Amended) A process for the preparation of the DMC catalyst[s] according to Claim 1, [characterized in that] comprising the steps of: (a) reacting an excess of at least one metal [salts] salt [in excess are reacted] in aqueous solution with at least one metal cyanide [salts] salt in the presence of the organic complexing ligand and the polycarbonate; [and the catalyst obtained is isolated, washed and then dried] (b) isolating the resultant catalyst; (c) washing the isolated catalyst; and (d) drying the catalyst.

Please add Claim 9.

--9. A process for the production of a polyether polyol comprising reacting an alkylene oxide onto a starter compound containing active hydrogen atoms, in the presence of the double-metal cyanide (DMC) catalyst of Claim 1. --

REMARKS

The title has been changed to make it correspond to that recited on the Assignment and Declaration and Power of Attorney.

Claim 8 has been cancelled and rewritten as new Claim 9 to place it in a form consistent with U.S. practices.

The above amendments to Claims 1-7 serve only to place the claims in proper form by removing multiple dependencies and correcting minor informalities. Support for new Claim 9 can be found in the specification on page 2, lines 6-10; page 9, lines 13-14; and working examples 7, 8 and 10. Working example 7 is found on page 17, lines 1-10, while working example 8 is found on page 17, lines 14-21, and, finally, working example 10 is found on page 18, lines 11-26. A new Abstract page is enclosed

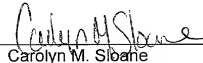
Applicants respectfully submit that no new matter has been added by these amendments.

In view of the preceding amendments and remarks, Applicants respectfully request an early action on the merits.

Respectfully submitted,

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By



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**IMPROVED DOUBLE-METAL CYANIDE CATALYSTS FOR THE
PRODUCTION OF POLYETHER POLYOLS**

Abstract of the Disclosure

The invention relates to novel, improved double metal cyanide (DMC) catalysts for the preparation of polyetherpolyols by the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms, the catalyst containing a double metal cyanide compound, an organic complexing ligand and 2 - 80 wt.% of a polycarbonate, based on the amount of catalyst.

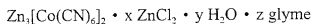
The novel, improved catalysts have markedly shortened induction times and simultaneously a greatly increased activity in the preparation of polyetherpolyols.

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Improved double metal cyanide catalysts for the preparation of polyetherpolyols

- 5 The invention relates to novel, improved double metal cyanide (DMC) catalysts for the preparation of polyetherpolyols by the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms.

- 10 Double metal cyanide (DMC) catalysts for the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms are known (cf. for example US 3 404 109, US 3 829 505, US 3 941 849 and US 5 158 922). The effect of using these DMC catalysts for the preparation of polyetherpolyols is particularly to reduce the proportion of monofunctional polyethers with terminal double bonds, called monools, in comparison to the conventional preparation of polyetherpolyols by
- 15 means of alkali metal catalysts such as alkali metal hydroxides. The resulting polyetherpolyols can be processed to high quality polyurethanes (e.g. elastomers, foams, coatings). DMC catalysts are conventionally obtained by reacting an aqueous solution of a metal salt with an aqueous solution of a metal cyanide salt in the presence of a low molecular organic complexing ligand, e.g. an ether. In a
- 20 typical catalyst preparation, for example, aqueous solutions of zinc chloride (in excess) and potassium hexacyanocobaltate are mixed and dimethoxyethane (glyme) is then added to the suspension formed. After filtration and washing of the catalyst with aqueous glyme solution, an active catalyst of the general formula



is obtained (cf. e.g. EP 700 949).

JP 4 145 123, US 5 470 813, EP 700 949, EP 743 093 and EP 761 708 have disclosed improved DMC catalysts which are capable of further reducing the proportion of monofunctional polyethers with terminal double bonds, in the

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Donna J. Veatch

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preparation of polyetherpolyols, by using tert-butanol as the organic complexing ligand (on its own or in combination with a polyether (EP 700 949, EP 761 708)). Furthermore, using the improved DMC catalysts reduces the induction time in the polyaddition reaction of the alkylene oxides with appropriate starter compounds and
5 increases the catalytic activity.

The object of the present invention is thus to provide further improved DMC catalysts for the polyaddition of alkylene oxides onto appropriate starter compounds, which, in comparison to the catalyst types known hitherto, have an appreciably
10 reduced induction time and simultaneously a markedly increased catalytic activity. This improves the economics of the process by shortening the total reaction times of the polyetherpolyol preparation. Ideally, by virtue of the increased activity, the catalyst can then be used in such small concentrations that an otherwise very costly catalyst separation is no longer necessary and the product can be used directly for
15 polyurethane applications. Surprisingly it has now been found that DMC catalysts containing 2 - 80 wt.% of a polycarbonate, based on the amount of catalyst, have markedly shortened induction times and simultaneously a greatly increased activity in the preparation of polyetherpolyols.

20 The present invention provides novel, improved double metal cyanide (DMC) catalysts comprising:

- a) a double metal cyanide compound and
- 25 b) an organic complexing ligand,

which are characterized in that they contain 2 to 80 wt.% of a polycarbonate, based on the amount of finished catalyst.

The catalysts according to the invention may also contain water, preferably 1 to 10 wt.%, and/or water-soluble metal salt, preferably 5 to 25 wt.%, from the preparation of the double metal cyanide compound.

- 5 The double metal cyanide compounds a) suitable for the catalysts according to the invention are the reaction products of a water-soluble metal salt and a water-soluble metal cyanide salt.

10 The water-soluble metal salt preferably has the general formula $M(X)_n$, M being selected from the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II) and Ni(II) are particularly preferred. X is an anion which is preferably selected from the group comprising halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, 15 oxalates and nitrates. The value of n is 1, 2 or 3.

Examples of suitable metal salts are zinc chloride, zinc bromide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) 20 nitrate. It is also possible to use mixtures of different metal salts.

The water-soluble metal cyanide salt preferably has the general formula $(Y)_a M'(CN)_b (A)_c$, M' being selected from the metals Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV) and V(V). M' is 25 particularly preferably selected from the metals Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II). The water-soluble metal cyanide salt can contain one or more of these metals. Y is an alkali metal ion or an alkaline earth metal ion. A is an anion selected from the group comprising halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates and 30 nitrates. Both a and b are integers (≥ 1), the values of a, b and c being chosen so as to ensure the electrical neutrality of the metal cyanide salt; c preferably has a value of

0. Examples of suitable water-soluble metal cyanide salts are potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

5 Examples of suitable double metal cyanide compounds a) which can be used in the catalysts according to the invention are zinc hexacyanocobaltate(III), zinc hexacyanoferrate(II), zinc hexacyanoferrate(III), nickel(II) hexacyanoferrate(II) and cobalt(II) hexacyanocobaltate(III). Other examples of suitable double metal cyanide compounds can be found e.g. in US 5 158 922 (column 8, lines 29 - 66). It is
10 preferable to use zinc hexacyanocobaltate(III).

The DMC catalysts according to the invention contain an organic complexing ligand b) because this increases e.g. the catalytic activity. Suitable organic complexing ligands are known in principle and are described in detail in the state of the art
15 indicated above (cf. e.g. US 5 158 922, column 6, lines 9 - 65). The complexing ligand is added either during the preparation of the catalyst or immediately after precipitation of the catalyst. The complexing ligand is conventionally used in excess. Preferred complexing ligands are water-soluble organic compounds containing heteroatoms, such as oxygen, nitrogen, phosphorus or sulfur, which are
20 capable of forming complexes with the double metal cyanide compound. Examples of suitable organic complexing ligands are alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and mixtures thereof. Preferred organic complexing ligands are water-soluble aliphatic alcohols, e.g. ethanol, isopropanol, n-butanol, isobutanol, sec-butanol and tert-butanol. Tert-butanol is particularly
25 preferred.

The DMC catalysts according to the invention contain the double metal cyanide compounds in amounts of 20 to 90 wt.%, preferably 25 to 80 wt.%, based on the amount of finished catalyst, and the organic complexing ligands in amounts of 1 to
30 30 wt.%, preferably 3 to 25 wt.%, again based on the amount of finished catalyst.

The DMC catalysts according to the invention contain 2 - 80 wt.% of a polycarbonate, based on the amount of catalyst. Preferred catalysts contain 5 - 50 wt.% of polycarbonate.

- 5 Polycarbonates suitable for the preparation of the catalysts according to the invention are higher molecular substances with the characteristic structural feature of the carbonic acid ester group, $-O-CO-O-$, as a repeat unit in the chain. They are normally obtained by the polycondensation of polyfunctional hydroxyl compounds (generally bishydroxyl compounds like alkanediols or bisphenols) with carbonic acid derivatives like phosgene or bis[chlorocarbonyloxy] compounds, carbonic acid diesters or urea. A further possibility is a three-component or multicomponent polycondensation of polyfunctional hydroxyl compounds (e.g. bisphenols) and carbonic acid derivatives with e.g. vinyl monomers or polymers, halogenobisphenols or bis(4-hydroxyphenyl)sulfanes, oxiranes, dicarboxylic acids or dicarboxylic acid dichlorides, phosphonic acid or phosphonic acid derivatives, or silicon compounds.
- 10 Other conventional methods of preparing polycarbonates consist in the polymerization of (macro)cyclic carbonic acid diesters, spirocyclic orthocarbonic acid tetraesters and unsaturated carbonic acid diesters, in the copolymerization of cyclic carboxylic acid diesters with other cyclic carbonic acid diesters, lactones or
- 15 lactams, and in the copolymerization of carbon dioxide with oxiranes or oxetanes.
- 20

- Methods of preparing polycarbonates are generally well known and are described in detail in for example "Houben-Weyl, Methoden der organischen Chemie" ("Houben-Weyl, Methods of Organic Chemistry"), volume E20, Makromolekulare Stoffe (Macromolecular Substances), 4th edition, 1987, pp. 1443 - 1457, "Ullmann's Encyclopedia of Industrial Chemistry", volume A21, 5th edition, 1992, pp. 207 - 215, and "Encyclopedia of Polymer Science and Engineering", volume 11, 2nd edition, 1988, pp. 648 - 718.
- 25

- 30 It is preferable to use aliphatic polycarbonates having hydroxyl end groups and average molecular weights below 12,000, as determined by measurement of the OH

number, which are generally prepared from polyfunctional aliphatic hydroxyl compounds (generally diols) by reaction with diaryl carbonate, dialkyl carbonate, dioxolanones, phosgene, bischlorocarbonic acid esters or urea.

- 5 It is particularly preferable to use aliphatic polycarbonate-diols with average molecular weights of 400 to 6000, as determined by measurement of the OH number, which are generally obtained from non-vicinal diols by reaction with diaryl carbonate, dialkyl carbonate, dioxolanones, phosgene, bischlorocarbonic acid esters or urea (cf. e.g. EP 292 772 and the documents cited therein).

10

The following non-vicinal diols are particularly suitable for this purpose: 1,4-butanediol, neopentyl glycol, 1,5-pentanediol, 2-methyl-1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, bis(6-hydroxyhexyl) ether, 1,7-heptanediol, 1,8-octanediol, 2-methyl-1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,4-bis-hydroxymethylcyclohexane, diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, oxyalkylation products of diols with ethylene oxide and/or propylene oxide and/or tetrahydrofuran, having molecular weights of up to 1000, preferably 200 - 700, and, in rarer cases, so-called "dimeric diols" obtainable by reduction of both the carboxyl groups of so-called "dimeric acids", which in turn are obtainable by the dimerization of

20

The diols can be used individually or in mixtures.

- 25 It is possible to use small amounts of higher boiling monofunctional alcohols such as phenylethyl alcohol, decanol, stearyl alcohol or lauryl alcohol.

Small amounts of trifunctional or higher functional alcohols, e.g. trimethylolethane, trimethylolpropane or pentaerythritol, can also be used for branching.

30

The following compounds can be used for reaction with the non-vicinal diols: diaryl carbonates such as diphenyl, ditolyl, dixylyl and dinaphthyl carbonate, dialkyl carbonates such as dimethyl, diethyl, dipropyl, dibutyl, diamyl and dicyclohexyl carbonate, dioxolanones such as ethylene carbonate and propylene carbonate,
5 hexanediol 1,6-bischlorocarbonic acid ester, phosgene and urea.

The reaction can be catalyzed in conventional manner by means of bases or transition metal compounds.

10 Both the use of the organic complexing ligand and the use of the polycarbonate are necessary for the preparation of a DMC catalyst with a reduced induction period and an increased activity (cf. Examples 7 - 8 and Comparative Examples 6 and 9). The catalyst composition is analyzed in conventional manner by means of elemental analysis and thermogravimetry.

15 The catalysts according to the invention can be crystalline, partially crystalline or amorphous. The crystallinity is analyzed in conventional manner by X-ray powder diffractometry.

20 The improved DMC catalysts according to the invention are prepared in conventional manner, in aqueous solution, by reacting metal salt (in excess) and metal cyanide salt in the presence of the organic complexing ligand and the polycarbonate.

25 The first step of this process is preferably to react the aqueous solution of the metal salt (e.g. zinc chloride, used in stoichiometric excess (at least 50 mol% based on the metal cyanide salt)) and the aqueous solution of the metal cyanide salt (e.g. potassium hexacyanocobaltate) in the presence of the organic complexing ligand (e.g. tert-butanol) to form a suspension containing the double metal cyanide
30 compound (e.g. zinc hexacyanocobaltate), excess metal salt, water and the organic complexing ligand.

The organic complexing ligand can be present in either one or both of the aqueous solutions, or it is added immediately to the suspension obtained after precipitation of the double metal cyanide compound. It has been found advantageous to mix the aqueous solutions and the organic complexing ligand with vigorous stirring.

5

The suspension formed is then treated with the polycarbonate, which is preferably used in a mixture with water and organic complexing ligand.

10

The catalyst containing the polycarbonate is isolated from the suspension by known techniques, e.g. centrifugation or filtration.

15

To increase the activity of the catalyst, it is advantageous if the isolated catalyst is then washed with an aqueous solution of the organic complexing ligand (e.g. by resuspension and subsequent re-isolation by filtration or centrifugation). This procedure makes it possible to remove for example water-soluble by-products like potassium chloride, which have an adverse effect on the polyaddition reaction, from the catalyst according to the invention.

20

The amount of organic complexing ligand in the aqueous washing solution is preferably between 40 and 80 wt.%. It is further advantageous to add some polycarbonate, preferably in the range between 0.5 and 5 wt.%, to the aqueous washing solution.

25

It is also advantageous to wash the catalyst more than once. This can be done e.g. by repeating the first washing process. It is preferable, however, to use non-aqueous solutions, e.g. a mixture of organic complexing ligand and polycarbonate, for further washing processes.

30

Finally, optionally after pulverization, the washed catalyst is dried at temperatures of 20 - 100°C and at pressures of 0.1 mbar to normal pressure (1013 mbar).

The invention further provides the use of the improved DMC catalysts according to the invention for the preparation of polyetherpolyols by the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms.

- 5 The alkylene oxides which are preferably used are ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. The synthesis of the polyether chains by alkoxylation can be carried out e.g. with only one monomeric epoxide, but can also be effected randomly or in blocks with 2 or 3 different monomeric epoxides. Further details can be found in "Ullmanns Encyclopädie der industriellen Chemie"
- 10 ("Ullmann's Encyclopedia of Industrial Chemistry"), English edition, 1992, volume A21, pages 670 - 671.

- Compounds with molecular weights of 18 to 2000 and 1 to 8 hydroxyl groups are used as the starter compounds containing active hydrogen atoms. Examples which
- 15 may be mentioned are ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, hexamethylene glycol, bisphenol A, trimethylolpropane, glycerol, pentaerythritol, sorbitol, cane sugar, degraded starch and water.

- As the starter compounds containing active hydrogen atoms, it is advantageous to
- 20 use those which have been prepared e.g. by conventional alkali metal catalysis from the above-mentioned low molecular starters and represent oligomeric alkoxylation products with molecular weights of 200 to 2000.

- The polyaddition of alkylene oxides onto starter compounds containing active
- 25 hydrogen atoms, catalyzed by the catalysts according to the invention, generally takes place at temperatures of 20 to 200°C, preferably in the range 40 to 180°C and particularly preferably at temperatures of 50 to 150°C. The reaction can be carried out at total pressures of 0 to 20 bar. The polyaddition can be carried out without a solvent or in an inert organic solvent such as toluene and/or THF. The amount of
- 30 solvent is conventionally 10 to 30 wt.%, based on the amount of polyetherpolyol to be prepared.

The catalyst concentration is chosen so as to allow good control over the polyaddition reaction under the given reaction conditions. The catalyst concentration is generally in the range 0.0005 wt.% to 1 wt.%, preferably in the range 0.001 wt.% to 0.1 wt.%, based on the amount of polyetherpolyol to be prepared.

The reaction times for the polyaddition are within the range from a few minutes to several days.

The molecular weights of the polyetherpolyols prepared by the process according to the invention are in the range 500 to 100,000 g/mole, preferably in the range 1000 to 50,000 g/mole and particularly preferably in the range 2000 to 20,000 g/mole.

The polyaddition can be carried out continuously, batchwise or semibatchwise.

The catalysts according to the invention generally require an induction time of a few minutes to several hours.

With the aid of the novel catalysts according to the invention, the induction times in the preparation of polyetherpolyols are markedly shortened in comparison to the DMC catalysts known hitherto.

The alkoxylation times are greatly reduced simultaneously because of the substantially increased activity.

This leads to a shortening of the total reaction times (sum of induction time and alkoxylation time) typically of 65 - 80% in comparison to the DMC catalysts known hitherto, thereby improving the economics of the process.

By virtue of their markedly increased activity, the catalysts according to the invention can be used in such low concentrations (15 ppm or less, cf. Example 10)

that, for use in polyurethane applications, it is generally possible to dispense with removal of the catalyst from the polyol without having an adverse effect on the qualities of the product.

Examples

Preparation of the catalyst

5 **Comparative Example 1**

Preparation of a DMC catalyst with tert-butanol as the organic complexing ligand and without the use of polycarbonate (catalyst A, synthesis according to JP 4 145 123).

10

A solution of 10 g (73.3 mmoles) of zinc chloride in 15 ml of distilled water is added to a solution of 4 g (12 mmoles) of potassium hexacyanocobaltate in 75 ml of distilled water, with vigorous stirring. A mixture of 50 g of tert-butanol and 50 g of distilled water is then added immediately to the suspension formed and the resulting mixture is subsequently stirred vigorously for 10 min. The solid is isolated by filtration, then stirred for 10 min with 125 g of a mixture of tert-butanol and distilled water (70/30; w/w) and filtered off again. Finally the solid is stirred for a further 10 min with 125 g of tert-butanol. After filtration the catalyst is dried to constant weight at 50°C and normal pressure.

20

Yield of dried pulverulent catalyst: 3.08 g

Elemental analysis:

cobalt = 13.6%, zinc = 27.35%, tert-butanol = 14.2%, (polycarbonate = 0%)

25

Example 2

Preparation of a DMC catalyst with tert-butanol as the organic complexing ligand and with the use of an aliphatic polycarbonate (catalyst B).

30

A solution of 12.5 g (91.5 mmoles) of zinc chloride in 20 ml of distilled water is added to a solution of 4 g (12 mmoles) of potassium hexacyanocobaltate in 70 ml of distilled water, with vigorous stirring (24,000 rpm). A mixture of 50 g of tert-butanol and 50 g of distilled water is then added immediately to the suspension formed and the resulting mixture is subsequently stirred vigorously (24,000 rpm) for 10 min. A mixture of 1 g of a triethylene glycol/tetraethylene glycol polycarbonate (molar ratio triethylene glycol/tetraethylene glycol = 1/1) of average molecular weight 1972 (determined by measurement of the OH number), 1 g of tert-butanol and 100 g of distilled water is then added and the resulting mixture is stirred (1000 rpm) for 3 min. The solid is isolated by filtration, then stirred (10,000 rpm) for 10 min with a mixture of 70 g of tert-butanol, 30 g of distilled water and 1 g of the above polycarbonate and filtered off again. Finally the solid is stirred (10,000 rpm) for a further 10 min with a mixture of 100 g of tert-butanol and 0.5 g of the above polycarbonate. After filtration the catalyst is dried to constant weight at 50°C and normal pressure.

Yield of dried pulverulent catalyst: 5.42 g

Elemental analysis and thermogravimetric analysis:

cobalt = 10.5%, zinc = 24.2%, tert-butanol = 13.3%, polycarbonate = 21.2%

Example 3

Preparation of a DMC catalyst with tert-butanol as the organic complexing ligand and with the use of an aliphatic polycarbonate (catalyst C).

As Example 2 except that:

a dipropylene glycol polycarbonate of average molecular weight 1968 (determined by measurement of the OH number) is used instead of the polycarbonate of Example 2.

Yield of dried pulverulent catalyst: 5.33 g

Elemental analysis and thermogravimetric analysis:

cobalt = 10.8%, zinc = 24.4%, tert-butanol = 20.2%, polycarbonate = 15.0%

5

Comparative Example 4

Preparation of a DMC catalyst with the use of polycarbonate and without tert-butanol as the organic complexing ligand (catalyst D).

10

A solution of 12.5 g (91.5 mmoles) of zinc chloride in 20 ml of distilled water is added to a solution of 4 g (12 mmoles) of potassium hexacyanocobaltate in 70 ml of distilled water, with vigorous stirring (24,000 rpm). A mixture of 1 g of the polycarbonate of Example 3 and 100 g of distilled water is then added immediately to the suspension formed and the resulting mixture is subsequently stirred vigorously (24,000 rpm) for 10 min. The solid is isolated by filtration, then stirred (10,000 rpm) for 10 min with a mixture of 1 g of polycarbonate and 100 g of distilled water and filtered off again. Finally the solid is stirred (10,000 rpm) for a further 10 min with a mixture of 0.5 g of polycarbonate and 100 g of distilled water. After filtration the catalyst is dried to constant weight at 50°C and normal pressure.

20

Yield of dried pulverulent catalyst: 4.72 g

Elemental analysis and thermogravimetric analysis:

cobalt = 10.7%, zinc = 18.2%, polycarbonate = 28.6%, (tert-butanol = 0%)

25

Comparative Example 5

Preparation of a DMC catalyst with tert-butanol as the organic complexing ligand and with the use of a polyether (catalyst E, synthesis according to EP 700 949).

30

A solution of 12.5 g (91.5 mmoles) of zinc chloride in 20 ml of distilled water is added to a solution of 4 g (12 mmoles) of potassium hexacyanocobaltate in 70 ml of distilled water, with vigorous stirring (24,000 rpm). A mixture of 50 g of tert-butanol and 50 g of distilled water is then added immediately to the suspension formed and the resulting mixture is subsequently stirred vigorously (24,000 rpm) for 10 min. A mixture of 1 g of polypropylene glycol of average molecular weight 2000 (OH number = 56 mg KOH/g), 1 g of tert-butanol and 100 g of distilled water is then added and the resulting mixture is stirred (1000 rpm) for 3 min. The solid is isolated by filtration, then stirred (10,000 rpm) for 10 min with a mixture of 70 g of tert-butanol, 30 g of distilled water and 1 g of the above polyether and filtered off again. Finally the solid is stirred (10,000 rpm) for a further 10 min with a mixture of 100 g of tert-butanol and 0.5 g of the above polyether. After filtration the catalyst is dried to constant weight at 50°C and normal pressure.

Yield of dried pulverulent catalyst: 6.23 g

Elemental analysis and thermogravimetric analysis:

cobalt = 11.6%, zinc = 24.6%, tert-butanol = 3.0%, polyether = 25.8%

Preparation of polyetherpolyols

General procedure

50 g of polypropylene glycol starter (molecular weight = 1000 g/mole) and 3 - 20 mg of catalyst (15 - 100 ppm, based on the amount of polyol to be prepared) are placed in a 500 ml pressure reactor under inert gas (argon) and heated to 105°C, with stirring. Propylene oxide (ca. 5 g) is then metered in all at once until the total pressure has risen to 2.5 bar. Further propylene oxide is then metered in only when an accelerated pressure drop is observed in the reactor. This accelerated pressure drop indicates that the catalyst is activated. The remaining propylene oxide (145 g) is then metered in continuously at a constant total pressure of 2.5 bar. When the

metered addition of propylene oxide is complete and a post-reaction time of 5 hours at 105°C has elapsed, volatile fractions are distilled off at 90°C (1 mbar) and then cooled to room temperature.

- 5 The polyetherpolyols obtained were characterized by determination of the OH number, the double bond content and the molecular weight distribution M_w/M_n (MALDI-TOF-MS).

10 The course of the reaction was followed by conversion/time curves (propylene oxide consumption [g] vs. reaction time [min]).

The induction times were determined from the point of intersection of the tangent at the steepest point on the conversion/time curve with the extrapolated baseline of the curve.

15 The propoxylation times which are decisive for the catalytic activity correspond to the period of time between catalyst activation (end of the induction period) and the end of the metered addition of propylene oxide.

20 The total reaction time is the sum of the induction time and the propoxylation time.

Comparative Example 6

Preparation of polyetherpolyol with catalyst A (100 ppm)

25

Induction time:	290 min
Propoxylation time:	165 min
Total reaction time:	455 min
Polyetherpolyol:	OH number (mg KOH/g): 28.5
	double bond content (mmoles/kg): 6
	M_w/M_n : 1.12

30

Example 7

Preparation of polyetherpolyol with catalyst B (100 ppm)

5	Induction time:	95 min
	Propoxylation time:	40 min
	Total reaction time:	135 min
	Polyetherpolyol:	OH number (mg KOH/g): 28.8
		double bond content (mmoles/kg): 6
10	M_w/M_n :	1.05

Example 8

Preparation of polyetherpolyol with catalyst C (100 ppm)

15	Induction time:	65 min
	Propoxylation time:	35 min
	Total reaction time:	100 min
	Polyetherpolyol:	OH number (mg KOH/g): 28.7
		double bond content (mmoles/kg): 6
20	M_w/M_n :	1.04

Comparative Example 9

25 Preparation of polyetherpolyol with catalyst D (100 ppm)

Induction time:	>700 min
Propoxylation time:	no activity

30 A comparison between Examples 7 - 8 and Comparative Example 6 makes it clear that, in the preparation of polyetherpolyols with the DMC catalysts according to the

invention, containing an organic complexing ligand (tert-butanol) and a polycarbonate, the induction times obtained are markedly reduced in comparison to those of a DMC catalyst containing only an organic complexing ligand (tert-butanol), and that the catalysts according to the invention simultaneously possess a greatly increased activity (detectable by the substantially shortened propoxylation times).

Comparative Example 9 shows that a DMC catalyst containing only a polycarbonate and no organic complexing ligand is inactive.

Example 10

Preparation of polyetherpolyol with catalyst C (15 ppm)

15	Total reaction time:	310 min
	Polyetherpolyol: OH number (mg KOH/g):	29.6
	double bond content (mmoles/kg):	6
	M_w/M_n :	1.06

20 Without removal of the catalyst, the metal content of the polyol is as follows: Zn = 4 ppm, Co = 2 ppm.

Example 10 shows that, by virtue of their markedly increased activity in the preparation of polyetherpolyols, the novel DMC catalysts according to the invention can be used in such small concentrations that it is possible to dispense with separation of the catalyst from the polyol.

Comparative Example 11

Preparation of polyetherpolyol with catalyst E (15 ppm)

5	Total reaction time:	895 min
	Polyetherpolyol: OH number (mg KOH/g):	29.8
	double bond content (mmoles/kg):	6
	M_w/M_n :	1.04

- 10 A comparison between Example 10 and Comparative Example 11 shows that the novel DMC catalysts according to the invention, containing an organic complexing ligand (tert-butanol) and a polycarbonate, are appreciably more active than highly active DMC catalysts known hitherto, containing an organic complexing ligand (tert-butanol) and a polyether (of comparable molecular weight to that of the
- 15 polycarbonate used in the catalysts according to the invention). The preparation of polyetherpolyols with the novel catalysts according to the invention is therefore possible in markedly shortened total reaction times.

Claims

1. Double metal cyanide (DMC) catalysts comprising:
 - 5 a) a double metal cyanide compound
 - and
 - b) an organic complexing ligand,
- 10 characterized in that they contain 2 to 80 wt.% of a polycarbonate, based on the amount of finished catalyst.
2. DMC catalysts according to Claim 1, characterized in that the double metal
- 15 cyanide compound is zinc hexacyanocobaltate(III).
3. DMC catalysts according to Claim 1, characterized in that the organic complexing ligand is tert-butanol.
- 20 4. DMC catalysts according to Claims 1 to 3, characterized in that they contain 5 to 50 wt.% of polycarbonate.
5. DMC catalysts according to Claims 1 to 4, characterized in that they contain
- 25 aliphatic polycarbonates having hydroxyl end groups and average molecular weights below 12,000, as determined by measurement of the OH number, which are obtainable by reacting polyfunctional aliphatic hydroxyl compounds with diaryl carbonate, dialkyl carbonate, dioxolanones, phosgene, bischlorocarbonic acid esters or urea.
- 30 6. DMC catalysts according to Claims 1 to 5, characterized in that they contain aliphatic polycarbonate-diols with average molecular weights of 400 to 6000,

as determined by measurement of the OH number, which are obtainable by reacting non-vicinal diols with diaryl carbonate, dialkyl carbonate, dioxolanones, phosgene, bischlorocarbonic acid esters or urea.

- 5 7. A process for the preparation of the DMC catalysts according to Claim 1, characterized in that metal salts in excess are reacted in aqueous solution with metal cyanide salts in the presence of the organic complexing ligand and the polycarbonate, and the catalyst obtained is isolated, washed and then dried.

10

8. Use of the DMC catalyst according to Claim 1 for the preparation of polyetherpolyols by the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms.

Improved double metal cyanide catalysts for the preparation of polyetherpolyols

Abstract

The invention relates to novel, improved double metal cyanide (DMC) catalysts for the preparation of polyetherpolyols by the polyaddition of alkylene oxides onto starter compounds containing active hydrogen atoms, the catalyst containing a double metal cyanide compound, an organic complexing ligand and 2 - 80 wt.% of a polycarbonate, based on the amount of catalyst.

The novel, improved catalysts have markedly shortened induction times and simultaneously a greatly increased activity in the preparation of polyetherpolyols.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

"IMPROVED DOUBLE-METAL CYANIDE CATALYSTS FOR THE PRODUCTION OF POLYETHER POLYOLS"

the specification of which is attached hereto,

or was filed on **December 10, 1998**

as a PCT Application Serial No. **PCT/EP98/08073**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

197 57 574.9
(Number)

German
(Country)

December 23, 1997
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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